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Title: Resin compositions

[Summary]

[Object] To obtain resins higher in mechanical strength and elongation characteristics.

[Constitution] A resin composition contains an acrylic polymer (a) of 1000 or more in numerical-average molecular weight having hydroxyl groups at both the ends, a polyisocyanate (b) and a glycol having at least one alkyl group with 1 to 20 carbon atoms, with 4 or 6 to 10 carbon atoms at the main chain, and having hydroxyl groups at both the ends.

Claims

[Claim 1] A resin composition, comprising

an acrylic polymer (a) of 1000 or more in number average molecular weight with hydroxyl groups at both the ends, a polyisocyanate (b), and at least one compound (c) selected from the following (c1) to (c5):

(c1) A glycol with at least one alkyl group with 1 to 20 carbon atoms, with 4 or 6 to 10 carbon atoms at the main chain, and with hydroxyl groups at both the ends

(c2) A compound represented by the following general formula (1):

[Chemical formula 1]



(where R¹, R², R⁴ and R⁵ stand for, respectively independently, a hydrogen atom or alkyl group with 1 to 20 carbon atoms; R³ stands for a hydrogen atom or alkyl group with 1 or 3 to 20 carbon atoms; and it does not happen that all of R¹, R², R³, R⁴ and R⁵ are hydrogen atoms.)

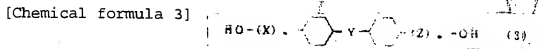
(c3): A compound represented by the following general formula (2):

[Chemical formula 2]



(where R¹, R², R⁴ and R⁵ stand for a hydrogen atom or alkyl group with 1 to 20 carbon atoms; R³ stands for an alkyl group with 1 to 20 carbon atoms; and Et stands for an ethyl group.)

(c4): A compound represented by the following general formula (3):



(where X and Z stand for, respectively independently, an alkyleneoxy group with 2 to 8 carbon atoms; Y stands for an alkylene group with 1 to 20 carbon atoms; and m and n stand for, respectively independently, an integer of 1 to 10.)

(c5): A compound represented by the following general formula (4):

[Chemical formula 4] —

(where X and Z stand for, respectively independently, an alkyleneoxy group with 2 to 8 carbon atoms; and m and n stand for, respectively independently, an integer of 1 to 10.)

[Claim 2] A resin composition, according to claim 1, wherein said compound (c) is at least one selected from a group consisting of 1,1-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1-methyl-1,3-propanediol, 1,1,3-trimethyl-1,3-propanediol, 2-ethyl-2-n-butyl-1,3-propanediol, 2-methyl-1,8-octanediol and 2,2-bis[4-(2-hydroxyethoxy)cyclohexyl]propane.

[Claim 3] A resin composition, according to claim 1 or 2, wherein the acrylic polymer (a) is obtained by polymerizing vinyl based monomers (d) with an acrylic monomer as an essential component, using substantially only an alcohol (e), an initiator (f) with an organic peroxide as an essential component, and an organic sulfonic acid compound (g):

[Claim 4] A resin composition according to claim 1 or 2, wherein the acrylic polymer (a) can be obtained by polymerizing vinyl

based monomers (d) with an acrylic monomer as an essential component, using substantially only alcohols (h) with a polyfunctional alcohol as an essential component, and an initiator (i) with hydrogen peroxide as an essential component.

[Claim 5] A resin composition, according to claim 1 or 2, wherein the acrylic polymer (a) is obtained by polymerizing vinyl based monomers (d) with an acrylic monomer as an essential component, using substantially only a compound (j) represented by the following general formula (5) and a radical polymerization initiator (k) while keeping said compound (j) existing in the reactor during reaction by an amount corresponding to 50 molar times or more of the amount of the radical polymerization initiator (k):

[Chemical formula 5]

(where R^6 and R^7 stand for, respectively independently, a divalent organic group; S stands for a sulfur atom; and l stands for an integer of 2 to 5.)

[Claim 6] A paint, comprising the resin compositions stated in any one of claims 1 through 5.

[Detailed description of the invention]

[0001]

[Industrial field of application] The present invention relates to resin compositions and paints.

[0002]

[Prior arts] Resin compositions containing a polyol and a polyisocyanate as essential components are excellent in mechanical properties and moldability, and widely used as various foams, elastomers, industrial parts, daily articles,

paints, adhesives, artificial leather, synthetic leather, etc. A resin composition using a polyol having an acrylic polymer as the main chain is suitable especially for applications requiring high heat-resistance, wetting-resistance, weather resistance, light resistance, etc. such as paints, artificial leather, synthetic leather, etc.

[0003] However, the acrylic polyol containing a monomer component with a hydroxyl group used in the resin composition has such problems that when the resin composition is used as a paint, it is insufficient in mechanical properties such as elongation and strength. Moreover, when the resin composition is used as artificial leather or synthetic leather, there exists such a problem as to be thermosetting, though it is required to be thermoplastic. To solve these problems, Japanese Patent Laid-Open No. 1994-107764 discloses a resin composition containing an acrylic polymer having hydroxyl groups at both the ends as a polyol component and further containing a low-molecular compound with two or more active hydrogen atoms in one molecule. The resin film obtained from the resin composition has been improved in elongation characteristics and stress (mechanical strength), but the improvement is still insufficient.

[0004]

[Problems to be solved by the invention] The problems to be solved by the present invention are to obtain resins higher in mechanical strength and elongation characteristics.

[0005]

[Means for solving the problems] The resin composition comprises an acrylic polymer (a) of 1000 or more in numerical average molecular weight having hydroxyl groups at both the ends, a

polyisocyanate (b), and at least one compound (c) selected from the following (c1) to (c5):

(c1) A glycol with at least one alkyl group with 1 to 20 carbon atoms, with 4 or 6 to 10 carbon atoms at the main chain, and with hydroxyl groups at both the ends

(c2) A compound represented by the following general formula (1):

[0006]

[Chemical formula 6]



[0007] (where R^1 , R^2 , R^4 and R^5 stand for, respectively independently, a hydrogen atom or alkyl group with 1 to 20 carbon atoms; R^3 stands for a hydrogen atom or alkyl group with 1 or 3 to 20 carbon atoms; and it does not happen that all of R^1 , R^2 , R^3 , R^4 and R^5 are hydrogen atoms.)

(c3): A compound represented by the following general formula (2):

[0008]

[Chemical formula 7]



[0009] (where R^1 , R^2 , R^4 and R^5 stand for a hydrogen atom or alkyl group with 1 to 20 carbon atoms; R^3 stands for an alkyl group with 1 to 20 carbon atoms; and Et stands for an ethyl group.)

(c4): A compound represented by the following general formula (3):

[0010]

[Chemical formula 8]



[0011] (where X and Z stand for, respectively independently, an alkyleneoxy group with 2 to 8 carbon atoms; Y stands for an alkylene group with 1 to 20 carbon atoms; and m and n stand for, respectively independently, an integer of 1 to 10.)

(c5): A compound represented by the following general formula (4):

[0012]

[Chemical formula 9]

(where X and Z stand for, respectively independently, an alkyleneoxy group with 2 to 8 carbon atoms; and m and n stand for, respectively independently, an integer of 1 to 10.)

It is preferable that said compound (c) is at least one selected from a group consisting of 1,1-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1-methyl-1,3-propanediol, 1,1,3-trimethyl-1,3-propanediol, 2-ethyl-2-n-butyl-1,3-propanediol, 2-methyl-1,8-octanediol and 2,2-bis[4-(2-hydroxyethoxy)cyclohexyl]propane.

[0014] It is preferable that the acrylic polymer (a) is obtained by polymerizing vinyl based monomers (d) with an acrylic monomer as an essential component, using substantially only an alcohol (e), an initiator (f) with an organic peroxide as an essential component, and an organic sulfonic acid compound (g). It is preferable that the acrylic polymer (a) is obtained by

polymerizing vinyl based monomers (d) with an acrylic monomer as an essential component, using substantially only alcohols (h) with a polyfunctional alcohol as an essential component, and an initiator (i) with hydrogen peroxide as an essential component.

[0015] It is preferable that the acrylic polymer (a) is obtained by polymerizing vinyl based monomers (d) with an acrylic monomer as an essential component, using substantially only a compound (j) represented by the following general formula (5) and a radical polymerization initiator (k) while keeping said compound (j) existing in the reactor during reaction by an amount corresponding to 50 molar times or more of the amount of the radical polymerization initiator (k):

[0016]

[Chemical formula 10]

[0017] (where R^6 and R^7 stand for, respectively independently, a divalent organic group; S stands for a sulfur; and l stands for an integer of 2 to 5.)

The paint of the present invention contains any of the above resin compositions.

The present invention is described below concretely.

Acrylic polymer (a)

The acrylic polymer (a) with hydroxyl groups at both the ends used in the present invention is described below.

[0018] The acrylic polymer (a) has hydroxyl groups at both the ends without fail, and the number of hydroxyl groups at the ends is one or more per end. The components of the acrylic polymer (a) are vinyl based monomers (d) with an acrylic monomer as an essential component. Only one vinyl based monomer (d), i.e.,

only an acrylic monomer can be used, or the vinyl based monomers (d) can also consist of an acrylic monomer and another vinyl based monomer copolymerizable with it. It is preferable that the amount of the acrylic monomer component is 40 wt% to 100 wt%, and that the amount of the other vinyl based monomer component copolymerizable with the acrylic monomer is 60 wt% to 0 wt%. (In this case, the total of these monomer components ~~are~~ is 100 wt%.)

[0019] The acrylic monomer of the present invention is not especially limited, and can be, for example, represented by any of the following general formulae (6) to (10).

[0020]

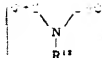
[Chemical formula 11]

[0021]

[Chemical formula 12]

[0022]

[Chemical formula 13]

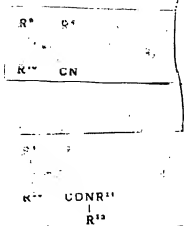


[0023]

[Chemical formula 14]

[0024]

[Chemical formula 15]



[0025] (In the above general formulae, R¹¹ and R¹³ stand for, respectively independently, a hydrogen atom, alkyl group, hydroxyalkyl group, halogenated alkyl group, aryl group or halogenated aryl group; R⁸, R⁹ and R¹⁰ stand for, respectively independently, a hydrogen atom, alkyl group, halogenated alkyl group, aryl group, halogenated aryl group or COOR¹¹; and R¹² stands for an alkyl group, halogenated alkyl group, aryl group or halogenated aryl group.)

The acrylic monomer can be selected from, though not limited to, (meth)acrylic acid; alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, dodecyl (meth)acrylate and stearyl (meth)acrylate; aryl (meth)acrylates such as benzyl (meth)acrylate; hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate; alkyl α-hydroxyalkylacrylates such as methyl α-hydroxymethylacrylate, ethyl α-hydroxymethylacrylate, butyl α-hydroxymethylacrylate, methyl α-hydroxyethylacrylate, ethyl α-hydroxyethylacrylate and butyl α-hydroxyethylacrylate; (meth)acrylic acid derivatives such as methoxyethyl

(meth)acrylate and ethylene oxide addition product of (meth)acrylic acid; perfluoroalkyl (meth)acrylates such as trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, triperfluoromethylmethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth)acrylate, 2-perfluorohexadecylethyl (meth)acrylate and perfluoroethylene; maleic anhydride, maleic acid, monoalkyl maleates and dialkyl maleates; fumaric acid, monoalkyl fumarates and dialkyl fumarates; maleimide and maleimide derivatives such as methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitro group-containing acrylic monomers such as acrylonitrile and methacrylonitrile; amide group-containing acrylic monomers such as acrylamide and methacrylamide, silicon-containing acrylic monomers such as γ -(methacryloyloxypropyl)trimethoxysilane. One or more of them can be used.

[0026] The vinyl based monomer copolymerizable with the acrylic monomer can be selected from conventional vinyl based monomers copolymerizable with acrylic monomers, for example, though not limited to, aromatic vinyl based monomers such as styrene,

vinyltoluene, α -methylstyrene, chlorostyrene, styrenesulfonic acid and its sodium salt; silicon-containing vinyl based monomers such as vinyltrimethoxysilane and vinyltriethoxysilane; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride, allyl alcohol, etc. One or more of these compounds can be used.

[0027] The number average molecular weight of the acrylic polymer (a) is 1,000 or more. Considering the reactivity of the ends and handling convenience (viscosity, etc.), the number average molecular weight of the polymer (a) is desirably, though not especially limited, in a range from 1,000 to 200,000, more desirably 1,000 to 50,000. If the number average molecular weight is less than 1,000, the resin obtained from the resin composition declines in elongation, etc.

[0028] The number of hydroxyl groups at the ends of the acrylic polymer (a) must be one or more per end. It is a necessary condition for production of a thermoplastic resin that each of the end groups has one or more hydroxyl groups. If the average number of end hydroxyl groups ($F_n(OH)$) of the acrylic polymer (a) is 2.1 or more, a thermosetting resin is produced, and in this case, the value of $F_n(OH)$ can be selected to suit the intended physical properties.

[0029] Since the resin composition of the present invention contains the acrylic polymer (a), the resin obtained from the resin composition is higher in heat resistance, wetting resistance, weather resistance, light resistance, etc. The resin composition of the present invention can also contain, as

required, another active hydrogen-containing high polymer, in addition to the polymer (a). The other active hydrogen-containing high polymer is not especially limited, and can be one or more selected from active hydrogen-containing polyethers (PEG, PPG, EO/PO copolymer and PTMG), active hydrogen-containing polyesters, active hydrogen-containing polybutadiene, active hydrogen-containing polycarbonates, active hydrogen-containing polyolefins, acrylic copolymers containing a monomer with active hydrogen, polymer polyols, etc.

[0030] The active hydrogen in the active hydrogen-containing high polymer refers to a functional group containing active hydrogen capable of reacting with an isocyanate group. The functional group can be selected from, though not limited to, hydroxyl group, amino group, imino group, carboxyl group, mercapto group, thiocarboxyl group, etc.

Acrylic polymer (a) production method

The method for producing the acrylic polymer (a) used in the present invention is not especially limited, but the acrylic polymer (a) can be produced by any of the following methods of A, B and C, preferably in view of the mechanical strength and elongation characteristic of the resin.

[0031] (A) Vinyl based monomers (d) with an acrylic monomer as an essential component are polymerized, using substantially only an alcohol (e), an initiator (f) with an organic peroxide as an essential component and an organic sulfonic acid compound (g), to obtain the acrylic polymer (a) (Production method stated in Japanese Patent Laid-Open No. 94-128311).

(B) Vinyl based monomers (d) with an acrylic monomer as an essential component are polymerized, using substantially only

alcohols (h) with a polyfunctional alcohol as an essential component and an initiator (i) with hydrogen peroxide as an essential component, to obtain the acrylic polymer (a) (Production method stated in Japanese Patent Laid-Open No. 94-100610).

(C) Vinyl based monomers (d) with an acrylic monomer as an essential component are polymerized, using substantially only a compound (j) represented by the following general formula (5) and a radical polymerization initiator (k), while keeping said compound (j) existing in the reactor during reaction by an amount corresponding to 50 molar times or more of the amount of the radical polymerization initiator (k), to produce the acrylic polymer (a) (Production method stated in Japanese Patent Laid-Open No. 93-262808).

[0032]

[Chemical formula 16]

[0033] (where R^6 and R^7 stand for, respectively independently, a divalent organic group; S stands for a sulfur atom; and l stands for an integer of 2 to 5.)

These methods are described below in detail. At first, the method A is described. The vinyl based monomers (d) with an acrylic monomer as an essential component can be selected from those enumerated for the components of the acrylic polymer (a). It is preferable that the amount of the acrylic monomer used as an essential component of the vinyl based monomers (d) is 40 wt% or more based on the total amount of the vinyl based monomers (d).

[0034] In the method A, the alcohol used as the alcohol (e) can also be a monofunctional alcohol with only one hydroxyl group in one molecule, or a polyfunctional alcohol with two or more hydroxyl groups in one molecule. It is also possible to use a monofunctional alcohol and a polyfunctional alcohol in combination. The monofunctional alcohol can be one or more selected from, though not limited to, ethyl alcohol, methyl alcohol, propyl alcohol, butyl alcohol, tertiary butyl alcohol, pentyl alcohol, higher alcohols with 12 to 14 carbon atoms, methoxyethanol, ethoxyethanol, propoxyethanol, ethylene glycol monoacetate, cyclohexanol, benzyl alcohol, phenethyl alcohol, etc. The polyfunctional alcohol can be one or more selected from, though not limited to, alkylene glycols such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2-pentanediol, 1,3-pentanediol, 1,4-pentanediol, neopentyl glycol, 1,5-pentanediol, 2,3-pentanediol, 2,4-pentanediol and 1,6-hexanediol; hydroquinone diethylol ether; ethylene glycol derivatives such as diethylene glycol and triethylene glycol; aliphatic polyfunctional alcohols such as sorbitol, cyclohexanediol and xylylenediol; glycerol, and glycerol fatty acid esters such as monoacetin, monoraulin, monoolein, monopalmitin and monostearin, and 1- or 2-substituted derivatives of glycerol such as glycerol monoallyl ether, thymyl alcohol and glycerol monomethyl ether; trimethylolpropane and its 1- or 2-substituted derivatives; pentaerythritol and 1- to 3-substituted derivatives of pentaerythritol such as pentaerythritol 2-oleate and pentaerythritol 2-stearate; sorbitan fatty acid esters; and saccharides such as

monosaccharides including erythritol, threose, ribose, arabinose, xylose, lyxose, allose, aldose, glucose, mannose, gulose, idose, galactose, talose, fructose, apiose, rhamnose, psicose, sorbose, ribulose and xylulose, and disaccharides including sucrose, maltose and lactose. Among these alcohols (e), when a thermoplastic polymer is intended, the use of a monofunctional alcohol is preferable, and when a thermosetting polymer is intended, the use of a polyfunctional alcohol is preferable. Among the alcohols (e), the use of ethylene glycol, 1,2-propanediol, 1,4-butanediol, trimethylolpropane, glycerol, pentaerythritol and sorbitol is especially preferable.

[0035] The alcohol (e) is not limited to those containing carbon, hydrogen and oxygen ~~only~~ as elements. For example, an alcohol containing nitrogen element or sulfur element in addition to the three elements can also be used. The nitrogen element-containing alcohol which can be used is not especially limited, and can be selected, for example, from amine based polyfunctional alcohols such as phenyldiethanolamine, triethanolamine, triisopropanolamine, diethanolamine, diisopropanolamine and trishydroxymethylaminomethane; and trishydroxycyanuric acid, etc.

[0036] The sulfur element-containing alcohol is, for example, an alcohol with a C=S bond, C-S-C bond, SO₂ bond, SO₃ bond, SH bond or S_n bond (n ≥ 2), etc. The sulfur element-containing alcohol which can be used is not especially limited, and can be selected, for example, from mercaptoethanol, methanesulfonylethanol, methylmercaptoethanol, ethylmercaptoethanol, thiodiethylene glycol, 2-hydroxyethyl disulfide, thiodiethylene glycol, ethylenebis-2-hydroxyethyl

sulfide, bishydroxyethylsulfone, N,N-bis(2-hydroxyethyl)taurine and its metal salts, laurylthiopropionic acid thiodiethanolamine salt, ethylene oxide addition product of thioethylene glycol, bis(2-hydroxyethyl)bisphenol-S, bis(2-hydroxyethyl)tetrabromobisphenol-S, bis(2-hydroxyethyl)tetramethylbisphenol-S, bis(2-hydroxyethyl)diphenylbisphenol-S, bis(2-hydroxyethyl)thiodiphenol, etc.

[0037] The ratio by weight of the alcohol (e) to the vinyl based monomers (d) used [alcohol (e) : vinyl based monomers (d)] is preferably 1 : 20 ~ 20 : 1, more preferably 1 : 10 ~ 10 : 1. The amount of the alcohol (e) is preferably 2 molar times or more, more preferably 50 molar times or more based on the amount of the initiator (f).

[0038] The organic peroxide used in the initiator (f) with an organic peroxide as an essential component is not especially limited, and can be selected, for example, from ketone peroxides such as methyl ethyl ketone peroxide, cyclohexanone peroxide, 3,3,5-trimethylcyclohexanone peroxide, methylcyclohexanone peroxide, methyl acetacetate peroxide and acetylacetone peroxide, peroxyketals such as 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-butylperoxy)cyclohexane, 2,2-bis(t-butylperoxy)cyclohexane, 2,2-bis(t-butylperoxy)octane and 2,2-bis(t-butylperoxy)butane, hydroperoxides such as t-butyl hydroperoxide, cumene hydroperoxide, di-isopropylbenzene hydroperoxide, 2-(4-methylcyclohexyl)-propane hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide and 1,1,3,3-tetramethylbutyl hydroperoxide, dialkyl peroxides such as di-t-butyl peroxide, t-butylcumyl peroxide, dicumyl peroxide, α,α' -

bis(5-butylperoxy-m-isopropyl)benzene and 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, diacyl peroxides such as acetyl peroxide, isobutyryl peroxide, octanoyl peroxide, decanoyl peroxide, lauroyl peroxide, 3,5,5-trimethylhexanoyl peroxide, succinic acid peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide and m-toluyyl peroxide, peroxydicarbonates such as di-isopropyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, di-n-propyl peroxydicarbonate, bis-(4-t-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, di-methoxyisopropyl peroxydicarbonate, di(3-methyl-3-methoxybutyl) peroxydicarbonate and di-allyl peroxodicarbonate, peroxy esters such as t-butyl peroxyacetate, t-butyl peroxyisobutyrate, t-butyl peroxyphthalate, t-butyl peroxyneodecanoate, cumyl peroxyneodecanoate, t-butyl peroxy-2-ethylhexanoate, t-butyl peroxy-3,5,5-trimethylhexanoate, t-butyl peroxyaurate, t-butyl peroxybenzoate, di-t-butyl peroxyisophthalate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, t-butyl peroxyphthalate, t-butyl peroxyisopropylcarbonate, cumyl peroxyoctoate, t-hexyl peroxyneohexanoate and cumyl peroxyneohexanoate, acetylcyclohexylsulfonyl peroxide, t-butyl peroxyallylcarbonate, etc. Especially cyclohexanone peroxide and benzoyl peroxide are suitable. One or more of these organic oxides can be used.

[0039] The initiator (f) with an organic peroxide as an essential component used in the method A can consist of an organic peroxide and a compound (I) capable of promoting polymerization when combined with the organic peroxide, or can be an organic peroxide only. The compound (I) can be selected from organic peroxide decomposing catalysts, reducing compounds

used for oxidation reduction reaction with the organic peroxide, surfactants, etc. That is, the initiator (f) with an organic peroxide as an essential component can be an organic peroxide alone or a mixture consisting of an organic peroxide as an essential component and one or more compounds capable of promoting polymerization selected from a group consisting of organic peroxide decomposing catalysts, reducing compounds and surfactants. The compound (I) capable of promoting polymerization when combined with an organic peroxide is described below concretely.

[0040] The organic peroxide decomposing catalyst used as the compound (I) is not especially limited, and can be selected, for example, from metal halides such as lithium chloride and lithium bromide; metal oxides such as titanium oxide and silicon dioxide; inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, perchloric acid and hydrobromic acid and their metal salts; carboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid and benzoic acid and their metal salts and esters; and heterocyclic amines such as pyridine, indole and its derivatives, imidazole and its derivatives and carbazole and its derivatives. One or more of them can be used.

[0041] The reducing compound used as the compound (I) for oxidation reduction reaction with the organic peroxide is not especially limited, and can be selected, for example, from organic metal compounds such as ferrocene; inorganic compounds such as inorganic metal compounds capable of generating metal ions of iron, copper, nickel or cobalt, etc., boron trifluoride ether addition product, potassium permanganate and perchloric

acid; sulfur-containing compounds such as sulfur dioxide, sulfites, mono- or di-alkyl sulfates, mono- or di-allyl sulfate, bisulfites, thiosulfates, sulfoxylates, benzenesulfinic acid and its substitution products, homologues of cyclic sulfinic acids including paratoluenesulfinic acid; mercapto compounds such as octylmercaptane, decylmercaptane, dodecylmercaptane, mercaptoethanol, α -mercaptopropionic acid, thioglycolic acid, thiopropionic acid, sodiumsulfopropyl α -thiopropionate and sodiumsulfoethyl α -thiopropionate; nitrogen-containing compounds such as hydrazine, β -hydroxyethylhydrazine and hydroxylamine; aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, n-butylaldehyde, isobutylaldehyde and isovalerianaldehyde; ascorbic acid, etc. One or more of them can be used.

[0042] The surfactant which can be used as the compound (I) can be selected from quaternary ammonium salts such as triethylbenzylammonium chloride, tetraethylammonium chloride, triethylbenzylammonium bromide, trioctylmethylammonium chloride, tributylbenzylammonium chloride, trimethylbenzylammonium chloride, N-laurylpyridinium chloride, trimethylbenzylammonium hydroxide, tetramethylammonium hydroxide, trimethylphenylammonium bromide, tetramethylammonium bromide, tetraethylammonium bromide, tetra-n-butylammonium bromide, tetra-n-butylammonium hydrogensulfate, N-benzylpicolinium chloride and N-lauryl-4-picolinium chloride; phosphonium salts such as tetrabutylphosphonium chloride; sulfonium salts such as trimethylsulfonium iodide; onium salts; polyoxyethylene-polypropylene oxide block copolymer; polyoxyethylene based surfactants such as polyoxyethylenesulfates; higher alcohols such as lauryl alcohol and stearyl alcohol; sulfuric acid esters

of these higher alcohols and metal salts of these sulfuric acid esters; higher fatty acids such as lauric acid and stearic acid and metal salts of these higher fatty acids, etc. One or more of them can be used.

[0043] Among the above surfactants, a surfactant having hydroxyl groups at both ends like polyoxyethylene-polypropylene oxide block copolymer is preferable because it can be incorporated into a crosslinked structure without exerting bad influence on the toughness, weather resistance and water resistance of the crosslinked product, and hence, there is no need of purification and removal. The initiator (f) is not limited to those enumerated above. For example, an organic peroxide or an organic peroxide and said compound (I) can be used together with a publicly-known radical initiator, e.g. such an azo based initiator as AIBN (azobisisobutyronitrile), or hydrogen peroxide, etc.

(0044) The amount of the initiator (f) used is decided by the molecular weight of the intended acrylic polymer (a), but generally, it is preferable to be 0.1 to 20 wt% based on the weight of the vinyl based monomers (d). The organic sulfonic acid compound (g) used in the method A is not especially limited and can be selected, for example, from aliphatic sulfonic acids such as methanesulfonic acid, ethanesulfonic acid, propane-sulfonic acid, propanesulfonic acid and octanesulfonic acid; aromatic sulfonic acids such as benzenesulfonic acid, benzene-disulfonic acid, naphthalenesulfonic acid and naphthalene-disulfonic acid; aromatic sulfonic acids with a nuclear substituent group such as chlorobenzenesulfonic acid, 1-naphthol-4-sulfonic acid, 2-naphthylamine-6-sulfonic acid, toluenesulfonic acid and

dodecylbenzenesulfonic acid; alicyclic sulfonic acids, etc. One or more of them can be used.

[0045] Among the above organic sulfonic acid compounds (g), especially methanesulfonic acid and dodecylbenzenesulfonic acid are preferable. Furthermore, an organic sulfonic acid compound with surface activity such as dodecylbenzenesulfonic acid is especially effective. The amount of the organic sulfonic acid compound (g) is preferably 0.05 to 10 wt% based on the weight of the entire polymerization system.

[0046] In the method A, during reaction, any other materials than the vinyl based monomers (d), alcohol (e), initiator (f) with an organic peroxide as an essential component and organic sulfonic acid compound (g) should not substantially be used in the reactor. Specifically, the amount of any other components than the vinyl based monomers (d), alcohol (e), initiator (f) with an organic peroxide as an essential component and organic sulfonic acid compound (g) should be kept at 10 wt% or less based on the weight of the whole. The amount of any other components than (d), (e), (f) and (g) is preferably 5 wt% or less, and it is most preferable that any other components than (d), (e), (f) and (g) are not contained at all.

[0047] The polymerization reactor used in the method A can be of batch type such as a general tank type reactor or kneader or of continuous type such as piston flow pipe type, two-screw extruder used depending on the viscosity of the polymer, or continuous kneader. A semi-batch type reactor can also be used without any problem at all. However, a tubular reactor, extruder or continuous kneader, etc. is preferable for such reasons that the concentration ratio of respective additives in

the reactor can be easily controlled by adding the respective additives halfway in the tube, that the residence time is constant and that the productivity is good. If the viscosity after polymerization is low, it is preferable to use a tubular reactor, and if relatively high, it is preferable to use an extruder or continuous kneader.

[0048] The wetted parts of these apparatuses should be made of any suitable material, generally SUS316, 304L, Hastelloy C, teflon or aluminum glass, etc. Among them, Hastelloy C, teflon, aluminum and glass are preferable, and Hastelloy C and glass are most preferable. The structure of the tubular reactor is not especially limited, and conventional tubular reactors of single tube type, multiple-tube type and a mixer free from moving part (produced by Noritake Company or Sumitomo Suzar (phonetic), etc.) can be used. In view of mixing efficiency and heat exchange efficiency, it is preferable to use a tubular reactor using a mixer free from moving parts. Also for the extruder or continuous kneader, any conventional extruder of single screw type, two-screw type, etc. can be used. In view of mixing efficiency and heat exchange efficiency, it is preferable to use a two-screw extruder or continuous kneader.

[0049] In the method A, the reaction can be effected at atmospheric pressure, but can also be effected in an autoclave or extruder, etc. under pressurization. The polymerization temperature in the method A is not especially limited either, and can be selected, without any problem, in a range from room temperature to about 200°C in which ordinary radical polymerization can be effected. The method B is described below.

[0050] The acrylic polymer (a) obtained by the method B has hydroxyl groups at both ends, and two or more hydroxyl groups at least at either of the ends. The vinyl based monomers (d) used in the method B are the same as the vinyl based monomers (d) used in the method A. The polyfunctional alcohol used in the alcohols (h) with a polyfunctional alcohol as an essential component is not especially limited as far as it is a compound with at least two hydroxyl groups in one molecule, and can be selected, for example, from alkylene glycols such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2-pentanediol, 1,3-pentanediol, 1,4-pentanediol, 1,5-pentanediol, 2,3-pentanediol, 2,4-pentanediol and 1,6-hexanediol; hydroquinone diethylol ether; ethylene glycol derivatives such as diethylene glycol and triethylene glycol; aliphatic polyfunctional alcohols such as sorbitol, cyclohexanediol and xylylenediol; glycerol, and glycerol fatty acid esters such as monoacetin, monoraulin, monoolein, monopalmitin and monostearin, and 1-substituted derivatives of glycerol such as glycerol monoallyl ether, thymyl alcohol, glycerol monomethyl ether and glycerol monoether; trimethylolpropane and its 1-substituted derivatives; pentaerythritol and 2-substituted derivatives of pentaerythritol such as pentaerythritol 2-oleate and pentaerythritol 2-stearate; sorbitan fatty acid esters; and saccharides such as monosaccharides including erythritol, threose, ribose, arabinose, xylose, lyxose, allose, aldose, glucose, mannose, gulose, idose, galactose, talose, fructose, apiose, rhamnose, psicose, sorbose, ribulose and xylulose, and disaccharides including sucrose, maltose and lactose. Among them, ethylene

glycol, 1,4-butanediol, trimethylolpropane, glycerol, pentaerythritol and sorbitol are preferable.

[0051] The polyfunctional alcohol is not limited to those containing carbon, hydrogen and oxygen alone as elements. For example, an alcohol containing nitrogen element or sulfur element in addition to the three elements can also be used. The nitrogen element-containing alcohol which can be used is not especially limited, and can be selected, for example, from amine based polyfunctional alcohols such as phenyldiethanolamine, triethanolamine, triisopropanolamine, diethanolamine, diisopropanolamine and trishydroxymethylaminomethane; and trishydroxycyanuric acid, etc.

[0052] The sulfur element-containing polyfunctional alcohol is, for example, an alcohol with a C=S bond, C-S-C bond, SO₂ bond or SO₃ bond, etc. In case of the method B, a polyfunctional alcohol with an SH bond or Sn bond ($n \geq 2$) cannot be used. The reason is as follows. Since an SH bond or Sn bond ($n \geq 2$) has high reactivity with a radical, the chain transfer constant is large, and the chain transfer reaction is liable to occur. Therefore, it is very difficult to introduce hydroxyl groups at both the ends of the polymer and to introduce two or more hydroxyl groups at least at either of the ends. Besides, the SH bond and Sn bond are liable to be oxidized by hydrogen peroxide, to wastefully consume hydrogen peroxide, and as a result, the decline of polymerization rate and the increase of molecular weight occur.

[0053] The sulfur element-containing polyfunctional alcohol which can be used is not especially limited as far as it does not have any of an SH bond or an Sn bond ($n > 2$), and it can be

selected, for example, from thiodiethylene glycol, ethylenebis-2-hydroxyethyl sulfide, bishydroxyethylsulfone, N,N-bis(2-hydroxyethyl)taurine and its metal salts, laurylthiopropionic acid thiodiethanolamine salt, ethylene oxide addition product of thioethylene glycol, bis(2-hydroxyethyl)bisphenol-S, bis(2-hydroxyethyl)tetrabromobisphenol-S, bis(2-hydroxyethyl)tetramethylbisphenol-S, bis(2-hydroxyethyl)diphenylbisphenol-S, bis(2-hydroxyethyl)thiodiphenol, etc.

[0054] One or more of these polyfunctional alcohols can be used. To adjust the solubility of the polyfunctional alcohol and the viscosity of the polymerization system, a monofunctional alcohol with only one hydroxyl group in the molecule can also be added. In this case, it is preferable that the amount of the monofunctional alcohol added is less than 50 wt% based on the weight of the alcohols (h) with a polyfunctional alcohol as an essential component.

[0055] The polyfunctional alcohol can be used as an aqueous solution in the reaction system. In this case, the concentration of the aqueous solution is not especially limited, but is preferably 50 wt% or more, considering the control of the molecular weight of the polymer and the reaction temperature. The initiator (i) with hydrogen peroxide as an essential component used in the method B can be either hydrogen peroxide alone or a combination of hydrogen peroxide and a compound (m) capable of promoting polymerization when combined with hydrogen peroxide. Hydrogen peroxide can be used as an industrially available aqueous solution, and the concentration is not especially limited. The compound (m) can be selected from

hydrogen peroxide decomposing catalysts, reducing compounds for oxidation reduction reaction with hydrogen peroxide, surfactants, etc. That is, the initiator (i) with hydrogen peroxide as an essential component can be either hydrogen peroxide alone or a mixture consisting of hydrogen peroxide as an essential component and one or more compounds capable of promoting polymerization, selected from a group consisting of hydrogen peroxide decomposing catalysts, reducing compounds and surfactants. The compound (m) capable of promoting polymerization when combined with hydrogen peroxide is concretely described below.

[0056] The organic peroxide decomposing catalyst used in the method B is not especially limited, and can be selected, for example, from metal halides such as lithium chloride and lithium bromide; metal oxides such as titanium oxide and silicon dioxide; inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, perchloric acid and hydrobromic acid and their metal salts; alkylbenzenesulfonic acids such as benzenesulfonic acid and p-toluenesulfonic acid and their metal salts; carboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid and benzoic acid and their metal salts and esters; and heterocyclic amines such as pyridine, indole and its derivatives, imidazole and its derivatives and carbazole and its derivatives.

[0057] The reducing compound used for oxidation reduction reaction with hydrogen peroxide in the method B can be selected from organic metal compounds such as ferrocene; inorganic compounds such as inorganic metal compounds capable of generating metal ions of iron, copper, nickel or cobalt, etc. in

water, boron trifluoride ether addition product, potassium permanganate and perchloric acid; sulfur-containing compounds such as sulfur dioxide, sulfites, mono- or di-alkyl sulfates, mono- or di-allyl sulfate, bisulfites, thiosulfates, sulfoxylates, benzenesulfinic acid and its substitution products, homologues of cyclic sulfinic acids including paratoluenesulfonic acid; mercapto compounds such as octylmercaptane, decylmercaptane, dodecylmercaptane, mercaptoethanol, α -mercaptopropionic acid, thioglycolic acid, thispropionic acid, sodiumsulfoethyl α -thiopropionate and sodiumsulfoethyl α -thiopropionate; nitrogen-containing compounds such as hydrazine, β -hydroxyethylhydrazine and hydroxylamine; aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, n-butylaldehyde, isobutylaldehyde and isovaleraldehyde; ascorbic acid, etc.

[0058] The surfactant which can be used in the method B can be selected from quaternary ammonium salts such as triethylbenzylammonium chloride, tetraethylammonium chloride, triethylbenzylammonium bromide, trioctylmethylammonium chloride, tributylbenzylammonium chloride, trimethylbenzylammonium chloride, N-laurylpyridinium chloride, trimethylbenzylammonium hydroxide, tetramethylammonium hydroxide, trimethylphenylammonium bromide, tetramethylammonium bromide, tetraethylammonium bromide, tetra-n-butylammonium bromide, tetra-n-butylammonium hydrogensulfate, N-benzylpicolinium chloride and N-lauryl-4-picolinium chloride; phosphonium salts such as tetrabutylphosphonium chloride; sulfonium salts such as trimethylsulfonium iodide; onium salts; alkylbenzenesulfonic acids such as p-toluenesulfonic acid and dodecylbenzenesulfonic

acid, and their metal salts; polyoxyethylene-polypropylene oxide block copolymer; polyoxyethylene based surfactants such as polyoxyethylenesulfates; higher alcohols such as lauryl alcohol and stearyl alcohol; sulfuric acid esters of these higher alcohols and metal salts of these sulfuric acid esters; higher fatty acids such as lauric acid and stearic acid and metal salts of these higher fatty acids, etc. One or more of them can be used.

[0059] Among the above surfactants, alkylbenzenesulfonic acids, onium salts and phosphorus-containing surfactants are preferable because they also have an effect for promoting the decomposition of hydrogen peroxide in addition to their surface activity. Especially dodecylbenzenesulfonic acid is more preferable. A surfactant having hydroxyl groups at both ends like polyoxyethylene-polypropylene oxide block copolymer is preferable because it can be incorporated into a crosslinked structure without exerting bad influence on the toughness, weather resistance and water resistance of the crosslinked product, and hence, there is no need of purification and removal.

[0060] In case of the method B, during the reaction, any other materials except the vinyl based monomers (d), alcohols (h) having a polyfunctional alcohol as an essential component and the initiator (i) having hydrogen peroxide as an essential component should not be substantially used in the reactor. Concretely, the amount of any other components except the vinyl based monomers (d), alcohols (h) having a polyfunctional alcohol as an essential component and the initiator (i) having hydrogen peroxide as an essential component should be kept at 10 wt% or less based on the weight of the whole.

The amount of any other components

than (d), (h) and (i) is preferably 5 wt% or less, and it is most preferable that any other components than (d), (h) and (i) are not contained at all.

[0061] The polymerization reactor used in the method B is the same as that used in the method A. The method C is described below. The vinyl based monomers (d) used in the method C are the same as the vinyl based monomers (d) used in the methods A and B.

[0062] The compound (j) represented by said general formula (5) is not especially limited, and can be selected, for example, from hydroxyalkyl di-, tri-, tetra- or penta-sulfides such as bis(hydroxymethyl) disulfide, bis(hydroxymethyl) trisulfide, bis(hydroxymethyl) tetrasulfide, bis(hydroxymethyl) pentasulfide, bis(2-hydroxyethyl) disulfide, bis(2-hydroxyethyl) trisulfide, bis(2-hydroxyethyl) tetrasulfide, bis(2-hydroxyethyl) pentasulfide, bis(3-hydroxypropyl) disulfide, bis(3-hydroxypropyl) trisulfide, bis(3-hydroxypropyl) tetrasulfide, bis(2-hydroxypropyl) disulfide, bis(2-hydroxypropyl) trisulfide, bis(2-hydroxypropyl) tetrasulfide, bis(4-hydroxybutyl) disulfide, bis(4-hydroxybutyl) trisulfide, bis(4-hydroxybutyl) tetrasulfide, bis(8-hydroxyoctyl) disulfide, bis(8-hydroxyoctyl) trisulfide and bis(8-hydroxyoctyl) tetrasulfide, and their ethylene oxide addition products and propylene oxide addition products; and di(2-hydroxyethyl) esters (ethylene oxide addition products) and di(hydroxypropyl) esters (propylene oxide addition products) of tri- and tetrasulfidodicarboxylic acids such as 2,2'-dithiodiglycolic acid, 2,2'-trithiodiglycolic acid, 2,2'-tetrathiodiglycolic acid, 3,3'-dithiodipropionic acid, 3,3'-trithiodipropionic acid, 3,3'-

tetrathiodipropionic acid, 3,3'-pentathiodipropionic acid, 4,4'-dithiodibutanoic acid, 4,4'-trithiobutanoic acid, 4,4'-tetrathiodibutanoic acid, 8,8'-dithiodioctanoic acid, 8,8'-trithiodioctanoic acid, 8,8'-tetrathiodioctanoic acid, 2,2'-dithiodibenzoic acid, 2,2'-trithiodibenzoic acid, 2,2'-tetrathiodibenzoic acid, 2,2'-dithiodinicotinic acid, 2,2'-trithiodinicotinic acid and 2,2'-tetrathiodinicotinic acid. One or more of them can be used.

[0063] The radical polymerization initiator (k) used in the method C is not especially limited, but can be selected, for example, from organic peroxides such as isobutyryl peroxide, cumyl peroxyneodecanoate, diisopropyl oxydicarbonate, di(n-propyl) peroxydicarbonate, di(2-ethoxyethyl) peroxydicarbonate, di(2-ethylhexyl) peroxydicarbonate, t-hexyl peroxyneodecanoate, t-butyl peroxyneodecanoate, t-hexyl peroxyipivalate, t-butyl peroxyipivalate, 3,3,5-trimethylhexanoyl peroxide, decanoyl peroxide, lauroyl peroxide, cumyl peroxyoctate, succinic acid peroxide, acetyl peroxide, t-butyl peroxy(2-ethylhexanoate), m-toluoyl peroxide, benzoyl peroxide, t-butyl peroxyisobutyrate, 1,1'-bis(t-butylperoxy)cyclohexane, t-butylperoxymaleic acid, t-butyl peroxy laurate, cyclohexanone peroxide, t-butyl peroxyisopropylcarbonate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, t-butyl peroxyacetate, 2,2'-bis(t-butylperoxy)butane, t-butyl peroxybenzoate, n-butyl-4,4'-bis(t-butylperoxy) valerate, di-(t-butylperoxy) isophthalate, methyl ethyl ketone peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, α,α' -bis(t-butylperoxy-m-isopropyl)benzene, t-butylcumyl peroxide, diisobutylbenzene hydroperoxide, di-t-butyl peroxide, p-menthane hydroperoxide, 2,5-dimethyl-2,5-di(t-

butylperoxy)hexyne-3,1,1,3,3,-tetramethylbutyl hydroperoxide, cumene hydroperoxide and t-butyl hydroperoxide; inorganic peroxides such as hydrogen peroxide, potassium persulfate, sodium persulfate and ammonium persulfate; azo compounds such as 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis(2-cyclopropylpropionitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2-methylbutyronitrile), 1,1'-azobis(cyclohexane-1-carbonitrile), 2-(carbamoylazo)isobutyronitrile, 2-phenylazo-4-methoxy-2,4-dimethylvaleronitrile, 2,2'-azobis(2-amidinopropane)dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutylamidine), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide], 2,2'-azobis(isobutylamide) dihydrate, 4,4'-azobis(4'-cyanopentanoic acid) and 2,2'-azobis(2-cyanopropanol); redox initiators such as hydrogen peroxide-Fe(II) salt, persulfate-sodium hydrogensulfite, cumene hydroperoxide-Fe(II) salt and benzoyl peroxide-dimethylaniline; and photosensitizers such as diacetyl, dibenzyl and acetophenone. One or more of them can be used.

[0064] In the method C, during reaction, the molar ratio $((j)/(K))$ of the compound (j) to the radical polymerization initiator (k) in the reactor must be kept at 50 or more, preferably 60 or more, most preferably 100 or more. In the method C, for polymerization, any other components than the compound (j), vinyl based monomers (d) and radical polymerization initiator (k) should not^{be} substantially ~~be~~ used. Specifically, the amount of any other components than the compound (j), vinyl based monomers (d) and radical polymerization initiator (k) should be kept at 10 wt% or less

based on the weight of the whole. The amount of any other components than (j), (d) and (k) is preferably 5 wt% or less, and it is most preferable that any other components than (j), (d) and (k) are not contained at all.

[0065] In the polymerization step of the method C, any polymerization method can be used, as far as the molar ratio ((j)/(k)) of the compound (j) to the radical polymerization initiator (k) in the reactor is kept at 50 or more during polymerization. For example, all of the compound (j), vinyl based monomers (d) and radical polymerization initiator (k) can be put into the reactor from the beginning for polymerization, or the respective ingredients can be supplied into the polymerization system from time to time during polymerization. As a further ~~other~~ method, at first at least some of the required amount of the compound (j) is put into the polymerization reactor beforehand, and the vinyl based monomers (d) and the radical polymerization initiator (k), and, as the case may be, the remaining amount of the compound (j) are fed for polymerization. In this case, since it is desirable that the radical polymerization initiator (k) is supplied as a solution of the vinyl based monomers (d), it is preferable to use an initiator sufficiently soluble in the vinyl based monomers (d) as the initiator (k). If the initiator (k) is little soluble in the vinyl based monomers (d), a solvent may be used as far as the object of the present invention is not impaired. In this case, if the vinyl based monomers (d) and the radical polymerization initiator (k) are continuously supplied to the compound (j), the polymerization reaction takes place mildly, and can be very easily controlled. However, the supply

of the vinyl based monomers (d) and the radical polymerization initiator (k) to the compound (j) can also be intermittent.

[0066] In the method C, the ratio of the compound (j) to the vinyl based monomers (d) in quantity is not especially limited, but it is preferable that the amount of the compound (j) is larger than that of the vinyl based monomers (d), to lessen the decrease in the number of hydroxyl groups at the ends per molecule of the polymer, $\text{Fn}(\text{OH})$, otherwise caused by the side reaction that the radicals produced by the initiator (k) are directly added to the vinyl based monomers (d) to initiate polymerization, without being chain-transferred to the compound (j). Specifically, the ratio $((j)/(d))$ by weight of the compound (j) to the vinyl based monomers (d) is preferably 0.5 or more, more preferably 1.0 or more.

[0067] The polymerization reactor used in the method C is the same as that used in the methods A and B. The polymerization pressure and temperature in the method C are also the same as in the methods A and B.

Compound (c)

The compound (c) used in the present invention is described below. The compound (c) is at least one compound selected from the following (c1) through (c5).

[0068] (c1): A glycol with at least one alkyl group with 1 to 20 carbon atoms, with 4 or 6 to 10 carbon atoms at the main chain, and with hydroxyl groups at both the ends

(c2): A compound represented by the following general formula (1):

[0069]

[Chemical formula 17]

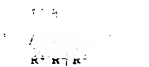


[0070] (where R^1 , R^2 , R^4 and R^5 stand for, respectively independently, a hydrogen atom or alkyl group with 1 to 20 carbon atoms; R^3 stands for a hydrogen atom or alkyl group with 1 or 3 to 20 carbon atoms; and it does not happen that all of R^1 , R^2 , R^3 , R^4 and R^5 are hydrogen atoms)

(c3): A compound represented by the following general formula (2):

[0071]

[Chemical formula 18]



[0072] (where R^1 , R^2 , R^4 and R^5 stand for a hydrogen atom or alkyl group with 1 to 20 carbon atoms; R^3 stands for an alkyl group with 1 to 20 carbon atoms; and Et stands for an ethyl group)

(c4): A compound represented by the following general formula (3):

[0073]

[Chemical formula 19]

[0074] (where X and Z stand for, respectively independently, an alkyleneoxy group with 2 to 8 carbon atoms; Y stands for an alkylene group with 1 to 20 carbon atoms; and m and n stand for, respectively independently, an integer of 1 to 10)

(c5): A compound represented by the following general formula (4):

[0075]

[Chemical formula 20]

[0076] (where X and Z stand for, respectively independently, an alkyleneoxy group with 2 to 8 carbon atoms; and m and n stand for, respectively independently, an integer of 1 to 10).

The compound (c1) is not especially limited, and can be selected, for example, from 1-ethyl-1,4-butanediol, 2-ethyl-1,4-butanediol, 1-butyl-1,6-hexanediol, 2-butyl-1,6-hexanediol, 2,3-dimethyl-1,6-hexanediol, 2-octyl-1,7-heptanediol, 2-methyl-1,8-octanediol, 3-ethyl-1,8-octanediol, 4-ethyl-1,9-nonanediol, 5-propyl-1,10-decanediol, 2,2-dimethyl-3-propyl-1,4-butanediol, etc.

[0077] The compound (c2) is not especially limited, and can be selected, for example, from 1-methyl-1,3-propanediol, 2-methyl-1,3-propanediol, 1-ethyl-1,3-propanediol, 1-propyl-1,3-propanediol, 2-propyl-1,3-propanediol, 1-butyl-1,3-propanediol, 2-butyl-1,3-propanediol, 1,1-dimethyl-1,3-propanediol, 1,2-dimethyl-1,3-propanediol, 1,1,3,2-trimethyl-1,3-propanediol, etc.

[0078] The compound (c3) is not especially limited, and can be selected, for example, from 2-ethyl-2-n-butyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, etc. The compound (c4) is not especially limited, but can be selected, for example, from products obtained by adding 1 to 20 moles of ethylene oxide to hydrogenated bisphenol A of 2,2-bis[4-(2-hydroxyethoxy)cyclohexyl]propane, etc., products obtained by

adding 1 to 20 moles of propylene oxide to hydrogenated bisphenol A of 2,2-bis[4-(2-hydroxypropoxy)cyclohexyl]propane, etc., products obtained by adding 1 to 20 moles of tetrahydrofuran to hydrogenated bisphenol A of 2,2-bis[4-(2-hydroxybutoxy)cyclohexyl]propane, etc., bis[4-(2-hydroxyethoxy)cyclohexyl]methane, 2,2-bis[4-(2-hydroxypropoxy)cyclohexyl]butane, 2,2-bis[4-(2-hydroxybutoxy)cyclohexyl]tetradecane, etc.

[0079] The compound (c5) is not especially limited, and can be selected, for example, from products obtained by 1 to 20 moles of ethylene oxide to hydrogenated bisphenol of bis[4-(2-hydroxyethoxy)cyclohexyl], etc., products obtained by adding 1 to 20 moles of propylene oxide to hydrogenated bisphenol of bis[4-(2-hydroxypropoxy)cyclohexyl], etc., and products obtained by adding 1 to 20 moles of tetrahydrofuran to hydrogenated bisphenol of bis[4-(2-hydroxybutoxy)cyclohexyl], etc.

[0080] Among the compounds (c1) to (c5), in view of the mechanical strength and elongation characteristic, the compound (c) is preferably at least one selected from a group consisting of 1,1-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1-methyl-1,3-propanediol, 1,1,3-trimethyl-1,3-propanediol, 2-ethyl-2-n-butyl-1,3-propanediol, 2-methyl-1,8-octanediol and 2,2-bis[4-(2-hydroxyethoxy)cyclohexyl]propane.

[0081] One or more of the above compounds can be used as the compound (c). As the compound (c), if a compound with a functional group not reacting with any isocyanate or with a functional group lower in reactivity than the hydroxyl group existing in the resin composition is used, the functional group not reacting with any isocyanate or the functional group lower

in reactivity than the hydroxyl group existing in the resin composition can be easily introduced into the resin structure.

[0082] The amount of the compound (c) in the resin composition of the present invention is preferably 0.1 to 200 parts by weight, more preferably 1 to 100 parts by weight against 100 parts by weight of the acrylic polymer (a). The amount can be properly decided, considering the application, required physical properties, etc. of the resin obtained from the composition.

Polyisocyanate (b)

The polyisocyanate (b) used in the present invention can be any known polyisocyanate and is not especially limited. It can be selected, for example, from those enumerated below.

[0083] Isocyanate compounds such as 1,4-phenylene diisocyanate, carbodiimide modified diphenylmethane diisocyanate, 4,4'-diisocyanate-3,3-dimethyldiphenyl, diphenyldimethylmethane-4,4'-diisocyanate, 1,3- or 1,4-cyclohexyl diisocyanate, 1,4-tetramethylene diisocyanate, bis(isocyanatemethyl)cyclohexane, tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,6-hexamethylene diisocyanate, xylene diisocyanate, metaxylylene diisocyanate, isopropylbenzene-2,4-diisocyanate, polymethylenepolyphenyl isocyanate, triphenylmethane triisocyanate, tris-4-phenyl isocyanate thiophosphate, 3,3',4,4'-diphenylmethane tetraisocyanate, addition reaction product of polypropylene glycol or triol and tolylene diisocyanate, addition reaction product of 1 mole of trimethylolpropane and 3 moles of tolylene diisocyanate, prepolymer between any of said active hydrogen-containing high polymers and a polyisocyanate, cyclohexanephenylene diisocyanate, chlorophenylene diisocyanate, naphthalene-1,5-diisocyanate, hydrogenated diphenylmethane

diisocyanate, hydrogenated tolylene diisocyanate, hydrogenated xylylene diisocyanate and isophorone diisocyanate; (the following trade names are phonetically spelled) burette polyisocyanate compounds such as Sumidule (produced by Sumitomo Bayer Urethane K.K.); polyisocyanate compounds with an isocyanurate ring such as Desmodule IL, HL (produced by Bayer A.G.) and Coronate EH (produced by Nippon Polyurethane Kogyo K.K.); adduct polyisocyanate compounds such as Sumidule L (produced by Sumitomo Bayer Urethane K.K.) and Coronate HL (produced by Nippon Polyurethane Kogyo K.K.). One or more of them can be used. A block isocyanate can also be used.

[0084] As a polyfunctional isocyanate compound to achieve more excellent weather resistance in the composition of the present invention, it is preferable to use an isocyanate compound without any aromatic ring such as hexamethylene diisocyanate, hydrogenated diphenylmethane diisocyanate or Sumidule N (produced by Sumitomo Bayer Urethane K.K.). The amount of the polyisocyanate (b) is preferably 0.5 to 3.0, more preferably 0.7 to 2.0, most preferably 0.8 to 1.5 in the equivalent ratio of NCO groups/active hydrogen atoms, and can be properly decided depending on the application, etc.

Resin composition

The resin composition of the present invention contains said (a), (b) and (c) as essential components.

[0085] To further promote the hardening of the resin composition, as required, a catalyst such as di-n-butyltin dilaurate, stannous octoate, triethylenediamine, diethylenediamine, triethylamine, metal naphthenate or metal octylate (lead octylate, etc.) can be used. Furthermore, as

required, a plasticizer such as dioctyl phthalate or dibutyl phthalate, modifier such as process oil or sticky resin, filler such as carbon black, white carbon, calcium carbonate, gypsum or vulcanized rubber powder, reinforcing agent such as carbon fibers, glass fibers organic fibers or asbestos fibers, oxidation stabilizer, antioxidant, coloring agent, flame retardant, etc. can also be added.

[0086] As required, a solvent can also be used. The solvent can be selected, for example, from ketones such as acetone, MEK, MIBK and cyclohexanone, aromatic hydrocarbons such as toluene, xylene and Solubesso (phonetic) 150, halogenated hydrocarbons such as chlorobenzene and trichlene, ethers such as THF and dioxane, esters such as cellosolve acetate, ethyl acetate and butyl acetate, and water. One or more of them can be used. The addition of water to the resin composition should be avoided since it reacts with the isocyanate, but it may be used to provide a water two-liquid resin for application with environmental protection intended. In this case, the kind and quantity of the isocyanate, catalyst, reaction temperature and reaction time must be carefully selected.

[0087] In the resin production process, the conventional one shot method, prepolymer method, etc. can be used. Furthermore, the order of reaction can also be optionally selected. If the compound (c) is added to a resin composition containing the acrylic polymer (a) with hydroxyl groups at both the ends and the polyisocyanate (b), a homogenous composition can be obtained probably because the compatibility between the acrylic polymer (a) and the compound (c) is high. Furthermore, since a homogeneous and transparent resin can be obtained because of

homogeneous (uniform) mixing during urethane production reaction, the resin can be improved in mechanical strength and elongation characteristics, in connection with the stress-strain characteristic of the resin.

[0088] The paint of the present invention contains said resin composition. The above properties of the resin composition are suitable for a paint composition, especially a paint composition for PCM (precoat metal) required to be excellent in contamination resistance and elongation while keeping the surface hardness. The resin composition of the present invention is excellent in mechanical strength and elongation characteristics. The resin composition of the present invention is very suitable as a raw material for artificial leather, synthetic leather, elastic wall materials, floor materials, waterproof agents for paint films, stickers, tackifiers, adhesives, binders, sealants, urethane foam (hard, semi-hard and soft), urethane RIM, UV-EB hardened resin, high solid paints, thermosetting elastomers, various molding materials, macrocellular, elastic fibers, fiber processing agents, plasticizers, sound absorbing materials, damping materials, surfactants, gel coating materials, resins for artificial marble, impact-resistant material for artificial marble, resin for laminated glass, reactive diluents, etc., and also as an additive for various resins and a raw material for various additives.

[0089]

[Examples] The present invention is described below concretely based on examples, but is not limited thereto or thereby. In the following examples, "parts" and "%" respectively mean "parts" by weight" and "wt".

Production of polymers

Polymers were produced according to the following Production Example A and Production Example B.

[0090] Production example A

A flask equipped with a stirrer, nitrogen introducing pipe, thermometer and reflux condenser tube was charged with 792.0 parts of ethylene glycol, and the atmosphere in the flask was substituted by nitrogen. While nitrogen gas was ^{being} gently blown in, the temperature was raised to 140°C. After the temperature in the reactor had been stabilized, a solution consisting of 0.8 part of p-toluenesulfonic acid and 10.0 parts of ethylene glycol was added at a time. Five minutes after addition, a solution with 158.4 parts of butyl acrylate, 315.5 parts of methyl methacrylate and 0.5 part of acrylic acid dissolved in 20.0 parts of cyclohexanone peroxide was added dropwise, taking 2 hours. After completion of dropwise addition, the mixture was immediately cooled, and after the temperature in the reactor had been lowered to 110°C, 0.54 part of sodium hydrogencarbonate was added. The mixture was kept stirred at 110°C for 20 minutes, to neutralize p-toluenesulfonic acid. The polymerization rate calculated from the remaining rates of butyl acrylate, methyl methacrylate and acrylic acid found by gas chromatography was 95%.

[0091] In succession, the temperature in the reactor was lowered to 80°C, and most of ethylene glycol was removed. Then, 1000 parts of toluene were added to dissolve the polymer, and the solution was transfused into a separating funnel, to remove the remaining ethylene glycol. The residue was washed by water 3 times, to obtain a toluene solution containing the polymer. The

water in the toluene solution was removed by azeotropic distillation of toluene and water, to obtain a toluene solution containing 40.0% of purified polymer A.

[0092] The number average molecular weight (M_n) of the purified polymer A was measured by the standard polystyrene conversion method using gel permeation chromatography, and found to be 7800. The average number of end hydroxyl groups ($F_n(OH)$) of the polymer A was calculated from the OH value = 39 obtained according to JIS K 1557 and from the measured number average molecular weight, and found to be 5.4 (moles/1 mole of the polymer).

[0093] Production example B

A flask equipped with a dropping funnel, stirrer, nitrogen introducing pipe, thermometer and reflux condenser was charged with 340.0 parts of xylene and 150.0 parts of n-butyl acetate, and they were heated and kept at 120°C while nitrogen ^{gas was being} ~~was~~ gently blown in. Furthermore, a mixture consisting of 8.0 parts of 2,2'-azobisisobutyronitrile (AIBN) and 10.0 parts of xylene, and a mixture consisting of 162.5 parts of butyl acrylate, 296.0 parts of methyl methacrylate, 37.0 parts of 2-hydroxyethyl methacrylate and 4.5 parts of acrylic acid were added dropwise, taking 3 hours. During the dropwise addition, the polymerization temperature was kept at 120±5°C.

[0094] After completion of dropwise addition, the mixture was kept stirred at the same temperature for further 4 hours, to complete polymerization, thus obtaining a solution containing 50.0% of the polymer B. The polymerization rate calculated from the solid content of the solution was 99%. The number average molecular weight (M_n) of the polymer B was measured by the

standard polystyrene conversion method using gel permeation chromatography, and found to be 7800. The average number of end hydroxyl groups ($\text{Fn}(\text{OH})$) of the polymer was calculated from the OH value = 34 obtained according to JIS K 1557 and from the measured number average molecular weight, and found to be 4.7 (moles/1 mole of the polymer).

Compatibility between respective polymer solutions and glycol

The polymers produced in the above were used in the following Examples 1 to 7 and Comparative Example 1.

[0095] Example 1

Five point zero parts of xylene, i-butyl acetate or cyclohexanone were put into sample bottles containing 5.0 parts each of the polymer A, and the respective mixtures were sufficiently stirred, to obtain homogeneous solutions. Into the solutions, 0.125 part of 1,1,3-trimethyl-1,3-propanediol was added as a glycol, and the mixtures were sufficiently stirred. Then, they were kept at 70°C for 1 hour, to make perfectly homogeneous solutions, and were allowed to stand ^(kept intact) at room temperature for about 15 hours. The respective solutions were visually observed to judge their homogeneity. The results are shown in Table 1. A homogeneous solution is expressed by o; a turbid solution, by Δ; and a phase separated solution, by x.

[0096] Examples 2 to 7

Experiments were conducted as described in Example 1, except that the glycols as shown in Table 1 were used, to observe compatibility.

Comparative example 1

Five point zero parts of xylene, i-butyl acetate or cyclohexanone were added into sample bottles containing 5.0

parts each of the polymer A, and the respective mixtures were sufficiently stirred, to make homogeneous solutions. Into the solutions, 0.125 part of ethylene glycol was added respectively as a glycol, and the solutions were sufficiently stirred. Then, operation as described in Example 1 was executed to observe compatibility.

[0097] From Table 1, it can be confirmed that the glycols used in Examples 1 to 7 were very good in solubility in the resin, compared to the glycol of Comparative Example 1.

[0098]

[Table 1]

Example	Glycol *1	Solvent *2		
		Xylene	Isobutyl acetate	Cyclohexanone
1	1,1,3-trimethyl-1,3-propanediol	o	o	o
2	1,1-dimethyl-1,3-propanediol	o	o	o
3	2,2-dimethyl-1,3-propanediol	o	o	o
4	1-methyl-1,3-propanediol	o	o	o
5	2-ethyl-2-n-butyl-1,3-propanediol	o	o	o
6	2-methyl-1,8-octanediol	o	o	o
7	2,2-bis[4-(2-hydroxyethoxy)cyclohexyl] propane	o	o	o
Comp 1	Ethylene glycol	x	Δ	Δ

As the polymer, the polymer A was used by 5 parts.

*1: Each glycol was used by 0.125 part.

*2: Each solvent was used by 5 parts.

[0099] Preparation of thermosetting resin compositions and resin films, and evaluation of their performance

The polymers produced as described before were used in the following Examples 8 to 14 and Comparative Examples 2 to 5.

Example 8

Twelve point six parts of a toluene solution containing 40% of the polymer A, 0.947 part of 1,1,3-trimethyl-1,3-propanediol as a glycol and 2.20 parts of a thinner as a solvent containing Solubesso 150, toluene, xylene, ethyl acetate and butyl acetate were put into a sample bottle, and sufficiently stirred. Furthermore, to obtain a resin composition and a resin film, Sumidule N-3500 (hexamethylene diisocyanate trimer produced by Sumitomo Bayer Urethane) as a trifunctional isocyanate was added as a polyisocyanate by an amount to achieve NCO/OH molar ratio of 1.0, and the mixture was sufficiently stirred, to obtain a resin composition.

[0100] The resin composition was applied onto releasing paper by an applicator, and the coated paper was put into a hot air dryer kept at a low humidity and cured in the presence of silica gel at 30°C for 17 hours. Then, the resin film was held between sheets of releasing paper, and punched by a dumb-bell die No. 2, to prepare a test piece. It was baked at 80°C for 3 hours. The thickness of the film was measured, and lines were marked. It was cured at 25°C and 65% relative humidity for 15 hours, to make a test piece. Its transparency was visually observed, and the stress-strain characteristic was measured using a tensile testing machine (Model 1185 produced by Instron) at a tensile speed of 2 mm/min at a load of 5 Kgwt and at 25°C and 65% relative humidity.

[0101] Examples 9 to 14

Resin compositions were obtained as described in Example 8, except that the glycols shown in Table 2 were used by amounts shown in Table 2. From the compositions, resin films were prepared, and their thicknesses were measured. Their

transparency was visually observed, and their stress-strain characteristics were measured by a tensile test. All of these operations were effected as described in Example 8.

[0102] Comparative example 2

Twelve point six parts of a toluene solution containing 40% of the polymer A, 0.50 part of ethylene glycol as a glycol and 2.20 parts of a thinner as a solvent were put into a sample bottle, and were sufficiently stirred. Then, 0.005 part of dibutyltin dilaurate was added as a catalyst, and the mixture was sufficiently stirred. Furthermore, to obtain a resin composition and a resin film, Sumidule N-3500 (hexamethylene diisocyanate trimer produced by Sumitomo Bayer Urethane) as a trifunctional isocyanate was added as a polyisocyanate, to achieve an NCO/OH molar ratio of 1.0, and the mixture was sufficiently stirred, to obtain a resin composition. From the composition, a resin film was prepared as described in Example 8, and its thickness was measured. Its transparency was visually observed, and its stress-strain characteristic was measured by a tensile test. All of these operations were effected as described in Example 8.

[0103] Comparative example 3

Twelve point six parts of a toluene solution containing 40% of the polymer A and 0.63 part of a thinner as a solvent were put into a sample bottle. Then, 0.005 part of dibutyltin dilaurate was added as a catalyst, and the mixture was sufficiently stirred. Furthermore, to obtain a resin composition and a resin film, Sumidule N-3500 (hexamethylene diisocyanate trimer produced by Sumitomo Bayer Urethane) as a trifunctional isocyanate was added as a polyisocyanate, to achieve an NCO/OH

molar ratio of 1.0, and the mixture was sufficiently stirred, to obtain a resin composition. From the composition, a resin film was prepared as described in Example 8, and its thickness was measured. Its transparency was visually observed, and its stress-strain characteristic was measured by a tensile test. All of these operations were effected as described in Example 8.

[0104] Comparative example 4

Ten point zero zero parts of a solution containing 50% of the polymer B, 0.716 part of 1,1,3-trimethyl-1,3-propanediol as a glycol and 4.41 parts of a thinner as a solvent were put into a sample bottle, and were sufficiently stirred. Then, 0.005 part of dibutyltin dilaurate was added as a catalyst, and the mixture was sufficiently stirred. Furthermore, to obtain a resin composition and a resin film, Sumidule N-3500 (hexamethylene diisocyanate trimer produced by Sumitomo Bayer Urethane) as a trifunctional isocyanate was added as a polyisocyanate, to achieve an NCO/OH molar ratio of 1.0, and the mixture was sufficiently stirred, to obtain a resin composition. From the composition, a resin film was prepared as described in Example 8, and its thickness was measured. Its transparency was visually observed, and its stress-strain characteristic was measured by a tensile test. All of these operations were effected as described in Example 8.

[0105] Comparative example 5

Ten point zero zero parts of a solution containing 50% of the polymer B and 3.33 parts of a thinner as a solvent were put into a sample bottle, and were sufficiently stirred. Then, 0.005 part of dibutyltin dilaurate was added as a catalyst, and the mixture was sufficiently stirred. Furthermore, to obtain a

resin composition and a resin film, Sumidule N-3500 (hexamethylene diisocyanate trimer produced by Sumitomo Bayer Urethane) as a trifunctional isocyanate was added as a polyisocyanate, to achieve an NCO/OH molar ratio of 1.0, and the mixture was sufficiently stirred, to obtain a resin composition. From the composition, a resin film was prepared as described in Example 8, and its thickness was measured. Its transparency was visually observed, and its stress-strain characteristic was measured by a tensile test. All of these operations were effected as described in Example 8.

[0106] The results of Examples 8 to 14 and Comparative Examples 2 to 5 are shown in Table 3 and Fig. 1.

[0107]

[Table 2]

<u>Examp.</u>	<u>Polymer (parts)</u>	<u>Glycol (parts)</u>	<u>Catalyst (parts)</u>	<u>Solvent (parts)</u>	<u>Isocyanate (parts)</u>
8	A*1 (12.6)	1,1,3-trimethyl-1,3- propanediol (0.947)	Dibutyltin dilaurate (0.005)	Thinner (2.20)	Sumidule N-3500 (3.78)
9	A*1 (12.6)	1,1-dimethyl-1,3- propanediol (0.834)	Dibutyltin dilaurate (0.005)	Thinner (2.20)	Sumidule N-3500 (3.78)
10	A*1 (12.6)	2,2-diethyl-1,3- propanediol (1.06)	Dibutyltin dilaurate (0.005)	Thinner (2.20)	Sumidule N-3500 (3.78)
11	A*1 (12.6)	1-methyl-1,3-propanediol (0.722)	Dibutyltin dilaurate (0.005)	Thinner (2.20)	Sumidule N-3500 (3.78)
12	A*1 (12.6)	2-ethyl-2-n-butyl-1,3- propanediol (1.28)	Dibutyltin dilaurate (0.005)	Thinner (2.20)	Sumidule N-3500 (3.78)
13	A*1 (12.6)	2-methyl-1,8-octanediol (1.28)	Dibutyltin dilaurate (0.005)	Thinner (2.20)	Sumidule N-3500 (3.78)
14	A*1 (12.6)	2,2-bis[4-(2-hydroxy- ethoxy)cyclohexyl]propane (2.63)	Dibutyltin dilaurate (0.005)	Thinner (2.20)	Sumidule N-3500 (3.78)
Compr. 2	A*1 (12.6)	Ethylene glycol (0.500)	Dibutyltin dilaurate (0.005)	Thinner (2.20)	Sumidule N-3500 (3.78)
Compr. 3	A*1 (12.6)	-	Dibutyltin dilaurate (0.005)	Thinner (0.63)	Sumidule N-3500 (0.67)
Compr. 4	B*1 (10.0)	1,1,3-trimethyl-1,3- propanediol (0.716)	Dibutyltin dilaurate (0.005)	Thinner (4.41)	Sumidule N-3500 (2.91)
Compr. 5	B*1 (10.0)	-	Dibutyltin dilaurate (0.005)	Thinner (3.33)	Sumidule N-3500 (0.555)

*1: 40% toluene solution

*2: 50% solution

[0408]

[Table 3]

Example	Transparency of resin film	Thickness of resin film (μm)	Stress-strain characteristic of resin film			
			Maximum tensile strength (10^4Pa)	Breaking strength (10^4Pa)	Inter-marked elongation (%)	Inter-chuck elongation (%)
8	Transparent		58	33.2	—	29
Compr. 2	Turbid		13	9	6	4
Compr. 3	Transparent		12	6	1.8	16
Compr. 4	Transparent		12	6	1.8	12
Compr. 5	Transparent		12	6	1.8	12

[0109] As shown in Fig. 1, the resin film obtained from the resin composition of Example 8 is very improved in elongation with the strength maintained, compared to Comparative Examples 2 to 5. Furthermore, a similar effect was confirmed also with the resin films of Examples 9 to 14.

Evaluation of performance of resin composition as paint for PCM

The polymer A produced in the above was used in the following Example 15.

[0110] Example 15

One hundred parts of a toluene solution containing 40% of the polymer A, 7.52 parts of 1,1,3-trimethyl-1,3-propanediol as a glycol, 17.44 parts of a thinner as a solvent, 0.02 part of dibutyltin dilaurate as a catalyst and 30.0 parts of Sumidule N-3500 (hexamethylene diisocyanate trimer produced by Sumitomo Bayer Urethane) ^{which is} as _A a trifunctional isocyanate as a polyisocyanate were sufficiently stirred, and the mixture was applied onto a PB-144-treated 0.5 mm thick standard test sheet (produced by Nippon Test Panel Osaka K.K. in conformity with JIS G 3141) to have a dry film thickness of 15 to 17 μ by a bar coater (No. 28), and baked at 80°C for 24 hours, to prepare a coated steel sheet. The pencil hardness of the paint film was

measured using a Uni pencil according to JIS K 5400, and found to be H. The coated steel sheet was bent from 180-degree 4T to 0T gradually, and the crack caused at the bent portion was observed by a 15-fold magnifying lens, to judge the processability (T bend). For example, if cracking occurs when the coated steel sheet is bent with three steel sheets with the same thickness held inside the bent portion, the processability is T bend 3T. In this case, the smaller the value of T bend, the higher the processability. The T bend of Example 15 was 1T. [0411] From the results of pencil hardness and processability (T bend), the paint film of Example 15 was found to have good processability.

[Brief description of the drawing]

[Fig. 1] Shows the stress-strain characteristics of the resin films obtained in Example 8 and Comparative Examples 2 to 5.

[Effects of the invention] If the resin composition of the present invention is used, the resin obtained is higher in mechanical strength and elongation characteristic. If the compound (c) contained in the resin composition of the present invention is at least one selected from a group consisting of 1,1-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1-methyl-1,3-propanediol, 1,1,3-trimethyl-1,3-propanediol, 2-ethyl-2-n-butyl-1,3-propanediol, 2-methyl-1,8-octanediol and 2,2-bis[4-(2-hydroxyethoxy)cyclohexyl]propane, the resin obtained can be further higher in mechanical strength and elongation characteristic. If the acrylic polymer (a) contained in the resin composition of the present invention is obtained by polymerizing the vinyl based monomers (d) with an acrylic monomer as an essential component, using substantially only the

alcohol (e), the initiator (f) having an organic peroxide as an essential component and the organic sulfonic acid compound (g) alone, the resin obtained can be made further higher in mechanical strength and elongation characteristics. If the acrylic polymer (a) contained in the resin composition of the present invention is obtained by polymerizing the vinyl based monomers (d) having an acrylic monomer as an essential component, using substantially the alcohol (h) alone having a polyfunctional alcohol as an essential component, and the initiator (i) having hydrogen peroxide as an essential component, the resin obtained can be made further higher in mechanical strength and elongation characteristics. If the acrylic polymer (a) contained in the resin composition of the present invention is obtained by polymerizing the vinyl based monomers (d) having an acrylic monomer as an essential component, using substantially the compound (j) represented by the general formula (5) and the radical polymerization initiator (k) alone while keeping the compound (j) existing in the reactor by an amount corresponding to 50 molar times or more of the radical polymerization initiator (k) during the reaction, the resin obtained can be made further higher in mechanical strength and elongation characteristics. The paint of the present invention is excellent in mechanical strength and elongation characteristics because it contains said resin composition(s).

